Removal of Arsenite and Arsenate Using Hydrous Ferric Oxide Incorporated into Naturally Occurring Porous Diatomite

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Introduction

Arsenic contamination in ground- and surface water is creating potentially serious environmental problems for human beings and other living organisms. Because of the recognition of this problem, a new arsenic limit of 10 ígL^{-1} will become effective in 2006 for drinking water systems in the United States. As a result of this new regulation, amall public water facilities will face heavy financial burdens. Arsenic contamination of groundwater is problematic throughout the world, where most people rely on tube wells as a source of drinking water. About 40-60%of the population (125 million people) of Bangladesh has been estimated to be adversely affected by arsenic-contaminated drinking water (*1*). Thus, there is an urgent demand for an economical, effective, and reliable technique that is capable of removing arsenic species to this new level. Adsorption is considered to be one of the most promising technologies because it is economical and easy to set up. Among several types of conventional sorbents, activated alumina with a proprietary additive, AAFS-50, was developed by Alcan to enhance arsenic removal (*2*). Sutherland et al. (*3*) reviewed different types of adsorption processes for arsenic removal in Bangladesh, evaluating the performance of nine technologies in terms of removal efficiency, cost, biological contamination, flow rate, reagent use, filtration time, and maintenance. Adsorption using AAFS-50 was found to be the best in relative performance among the nine technologies because of its high removal efficiency and flow rate (*3*, *4*). However, it was more expensive for both initial and ongoing operating costs than other reported technologies (*4*).

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(HFO) incorporated porous naturally occurring diatomite described in this study are environmentally acceptable, costeffective, and simple. As a porous supporting material, diatomite (diatomaceous earth) is a lightweight sedimentary rock composed mainly of silica microfossils of aquatic unicellular algae, consisting of various pores with up to 80-90% voids (*5*). Diatomite has been approved as a food-grade material by the U.S. Food and Drug Administration (FDA) and is stable in contact with liquids given that it originates and is produced from seas or lakes. Because of its high pore volume and surface area, as well as its low density, diatomite has found several industrial applications not only for the adsorption of inorganic and organic pollutants, but also for several other techniques (*6*, *7*). Yang et al. used two different local diatomites to find the relationship between the amount of urokinase adsorbed and the change in isoelectrical point (IEP) for sorption media (*7*). Al-degs et al. tried to modify the surface of diatomite with manganese oxide to remove lead ions in solution. Mn-modified diatomite was found to have an adsorption capacity of _100 mg of lead ions g^{-1}, because of an increase in surface area and negatively charged surface (*8*). ADI developed iron-impregnated diatomite (ADImedium G2) for arsenic removal (*9*), in which calcined diatomite (30 _ 60 mesh) and iron chloride were used as the supporting medium and iron precursor, respectively. Their preparation includes a pH increase to at least 9.0 with a highly alkaline solution (10 N sodium hydroxide). The iron solution that remained in excess should be properly treated, and there is a maximum limit of iron impregnation percentage (5-30% based on the mass of diatomite).

Hydrous ferric oxide (HFO) has been extensively studied as a promising adsorption material for removing both arsenate and arsenite from aqueous media because of its high isoelectric point (IEP)8.1) (*10*)andselectivity for arsenic species. However, several iron oxides includingHFOaremade as suspensions in aqueous solution and are available only as fine powders. Therefore, it is not suitable to use these fine powders in column applications because of their low hydraulic conductivity (*11*). To overcome this disadvantage, HFOgranulation techniques have been developed. Granular ferric hydroxide (GFH) was synthesized from ferric chloride solution by neutralization and precipitation with sodium hydroxide, followed by centrifugation and granulation under high pressure (*12*, *13*). GFH shows poor mechanical strength to create fine particles, causing a significant headloss pressure

within a short operating time (*13*). Because of its high diffusion limits, the adsorption capacity for arsenic is reduced by 50% when larger-sized materials (1-2 mm) are used (*13*).

To overcome these disadvantages of ADI medium G2 and GFH, an incipient wetness impregnation method was developed to disperse and incorporate nanoscale HFO homogeneously in the pores of diatomite using a vortex mixer. Compared to the preparation methods of other media, this technique is simple and economical because fewer steps and a smaller volume of precursor solution are needed for medium preparation. In addition, there is no iron solution remaining in excess that should be treated. The objectives of this study were (1) to incorporate active HFO homogeneously into the pores of diatomite through an incipient wetness impregnation technique; (2) to evaluate the arsenic adsorption capacities of themediumproduced by examining the adsorption edges and pH-controlled differential column batch reactor (DCBR) and small-scale column tests and comparing the performance with that of a conventional medium, AAFS-50; and finally (3) to understand the adsorption behavior of the medium through physicochemical characterizations and surface complexation modeling.

Methodology

Incorporation of Iron Oxide into Diatomite. A precursor of iron oxide, iron nitrate nonahydrate [$Fe(NO_3)_3â9H_2O$], was incorporated into the pore surface of granular-size porous diatomite (Harborlite mesh 10 _ 12) that mainly consists of aluminum oxide (12.8%, w/w) and silica (76.8%, w/w). The following coating procedure was developed to impregnate iron precursor into pore structures of diatomite as homogeneously as possible: (1) Dissolve iron precursor in deionized water at a given concentration to give a final volume of the metal-dissolved solution of 15 mL. (2) Place 10 g of dried diatomite into a 500-mL Teflon bottle. (3) Disperse the iron precursor solution over the diatomite using a 5-mL micropipet. (4) After closing the cap, place the Teflon bottle on a vortex mixer (Genie) and vigorously mix at _2000 rpm for 5 min to obtain a homogeneous mixing of the iron solution and diatomite (homogeneity was judged by observing the change of red color distribution on the medium). (5) Dry the solids at room temperature for 1 day. (6) Calcine the material in an oven with a programmed temperature profile that started from room temperature and increased at a rate of 1.0

°C/min to 90 °C, which was then held for 24 h. After calcination, the solids were stored in a vacuum chamber. The solids were then washed with deionized water until the conductivity of the filtrate was close to that of deionized water. The conductivity tests followed the procedure described by Jang et al. (*14*). In this study,25%iron-incorporated diatomite [designated Fe (25%)-diatomite] was prepared and used for subsequent experiments.

Characterization. Using a Stoe high-resolution X-ray diffractometer (Microphotonics, Allentown, PA) with Cu KR radiation (40 kV, 25 mA), X-ray diffraction patterns over a wide range of angles (10-70°) were acquired for plain diatomite and Fe (25%)-diatomite. For scanning electron microscopy with energy-dispersive X-ray(SEM-EDX)analysis, several samples were coated with gold using a Denton Vacuum Dest II sputter machine. Then, the sample plug was introduced into the SEM (JEOL JSM-6100) to obtain images at different scales, and energy-dispersive X-ray (EDX) tests were conducted to find the degree of homogeneous dispersion of iron in different sizes of particles.N_2 gas adsorptiondesorption isotherms were performed at 77 K using a Micromeritics ASAP 2000 analyzer (Norcross, GA).

Arsenic Sorption Edges and Surface Complexation Modeling. Sodium arsenate ($Na_2HAsO_4â7H_2O$, Sigma) and sodium arsenite ($NaAsO_2$, 1000 mg L^{-1} As, Fluka) solution were used without any modification as the arsenate and arsenite stock solutions, respectively. A stock solution of 0.01 M $NaNO_3$ in deionized water was prepared. The solution of a predetermined volume was poured into a polyethylene bottle. A small volume of arsenic stock solution was added to achieve the target arsenic concentration. Then, the pH was adjusted to 3-11 for each arsenic solution with an automatic pH titrator, using small volumes of acid (HNO_3, 0.1 M) and base (NaOH, 0.1 M) stock solutions. Meanwhile, AAFS-50 (Alcan mesh 28_48) and Fe (25%)-diatomite were homogeneously pulverized to be smaller than 75 *í*m (sieve no. 200) and suspended at a concentration of 10 g L^{-1} in $NaNO_3$ (0.01 M) solution. While the suspension was being stirred with a magnetic stirrer, a predetermined volume of suspension was added to the arsenic solution. All samples were mixed in a rotary shaker at 250 rpm and 20 (0.5 °C. After 8 h of shaking, the pH of the samples was readjusted to 3-11 with the automatic pH titrator. All samples were then shaken again in the rotary shaker until equilibrium was

reached.

X-ray absorption fine structure (XAFS) and FTIR spectroscopic studies have recently provided evidence for the formation of inner-sphere adsorption complexes of oxy anions on hydrous ferric oxide surfaces (*15*, *16*). Because of this, arsenic adsorption behaviors of various solids have been investigated using the constant capacitance model (CCM) in the intrinsic surface complexation modeling (*17-19*). The computer program FITEQL 4.0 (*20*) was used to optimize the intrinsic surface complexation constants, reactive surface site densities, and surface hydrolysis constant. In this study, the one-site adsorption model was employed. Constants for protonation of aqueous arsenic species were obtained from MINEQL 4.5 (*21*). The surface reaction and equilibrium expression for intrinsic surface complexation of arsenic sorption on the medium are summarized in the Supporting Information (Table S1). To optimize all parameters, the sequential optimization strategy was applied (*22*). First, five adjustable parameters (two surface hydrolysis constants, two surface complexation constants, and one hydroxyl density) were optimized to achieve satisfactory fits of the CCM to the experimental data of arsenite sorption edges. However, because FITEQL would not convergewhenthe five adjustable parameters were optimized simultaneously, a sequential optimization scheme was used where surface hydrolysis constants were optimized first. Then, a separate optimization of the surface hydroxyl density and two arsenite surface complexation constants was performed while holding the optimized surface hydrolysis constants fixed. Then, the surface hydrolysis constants and hydroxyl density were selfconsistent for optimizing the three surface complexation constants of arsenate sorption edges. This approach yielded the best fits of the model to experimental data based on values of the weighted sum of squares divided by the degrees of freedom (WSOS/DF) calculated in FITEQL 4.0.

pH-Controlled Differential Column Batch Reactor (DCBR) Tests. Because it was not possible to conduct conventional kinetic tests in suspension given that Fe (25%)-diatomite floats (its bulk density is 0.25 g cm^{-3}), pH-controlled differential column batch reactor (DCBR) tests were conducted. In previous work, Badruzzaman et al. (*23*) did not control the pH of arsenic feed solution during DCBR operation. This test might havesomeerrors in arsenic removal speeds and capacities because pH is one of the most

significant parameters in affecting arsenic species and active surface sites of metal oxide. Thus, it is important to control the pH of the arsenic feed solution by use of an automatic pH controller. In this study, arsenite or arsenate solution was circulated through a DCBR at a constant pH from a mixed feed container (1.0 L) with 3.3minofemptybed contact time (EBCT). The schematic and methodology of the DCBR test are presented in the Supporting Information (Figure S1).

A pseudo-second-order kinetic equation was found to fit well for much of the chemisorption using heterogeneous materials (*24*, *25*). All of the kinetic data from our experiments were fitted with a pseudo-second-order kinetic model to estimate the rate constants, initial sorption rates, and arsenic sorption capacities on different media. The pseudo-secondorder kinetic rate equation is well described by Jang et al. (*14*). Along with the pseudo-second-order kinetic model, the shrinking-core model (*26*) was used to estimate mass-transfer characteristic parameters of arsenic removal, assuming that arsenic adsorption is a fast reaction relative to diffusion. Considering external film diffusion and intraparticle diffusion control, this model had been applied to find the apparent diffusivity of metal ions in various adsorbents by fitting equations to experimental data (*26*-*28*). For a process controlled by the diffusion of arsenic through the liquid film (film diffusion control), the extent of the arsenic adsorption as a function of time is given by the expression.